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Microstructural Analysis of the Brass Seat of a Valve from the 1907 Steam Tug "Hercules"

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The steam tug Hercules was an ocean-going and bay tug for 55 years before being retired. It is now being restored by the National Park Service (as of 1993 printing of this article). A broken steam valve was obtained for microstructural examination. The body was gray cast iron, and the stem and seat were brass. The examination centered on corrosion of the brass components. The seat and shaft were α brass, with a hardness of 64 and 79 DPH, respectively. A nut held the shaft onto the seat and was α-β brass with a hardness of 197 DPH. Welded on the end of the shaft was a ring of hard (DPH 294) α-β brass, which seated against the nut. The brass seat and stem showed little corrosion. However, the α-β brass nut and welded tip show extensive dezincification. This process of removal of Zn and the retention of Cu began in the high Zn β phase, but eventually both phases were attacked. The depth of penetration was consistent with dezincification rates reported in the literature for such brasses in salt water if the valve had been in service about 55 years.

Keywords: brass alloy, dezincification, failure analysis, gate valve, gray cast iron, naval brass, steam valve

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Introduction

Hercules is an ocean-going tug built in New Jersey in 1907 for a San Francisco company. This hardworking type of craft reached its peak development at the turn of the century because of her design. A deep, narrow hull and a 1000 hp, triple expansion engine were designed to provide sure steering and steady pulling ability even in high seas. The Hercules served for 55 years, first as an ocean-going tug and, beginning in 1924, as a San Francisco Bay tug. She went out of service in 1962. In 1986, she was acquired by the California State Park Foundation and was brought to the National Park Service. She was designated a National Historic Landmark in 1986 (Ref 1).

The Hercules is currently undergoing extensive restoration. This has required replacement of inoperable parts. We were able to obtain a broken gate valve for examination (Fig. 1). The outside was made of gray cast iron, and the outlet port was broken off. The valve shaft and seat were of brass, and it is this part that was examined microstructurally and its features are reported in this paper. Of particular interest are the regions of corrosion by dezincification.

Experimental Procedures

The valve stem was removed for examination (Fig. 2). The seat and parts near it show extensive corrosion, but the stem outside the valve is relatively unaffected. The valve seat part was removed and mounted in epoxy, then cut in a plane through the shaft axis with a high-speed cut-off wheel using copious water for cooling.

The metallographic samples were ground and polished using standard techniques (Ref 2). They were etched for 15 to 20 s by swabbing with a solution of 10 g Cr_2O_3, 12.5 g NH_4Cl_2, 12.5 mm H_2SO_4 and 750 mL water. The samples were

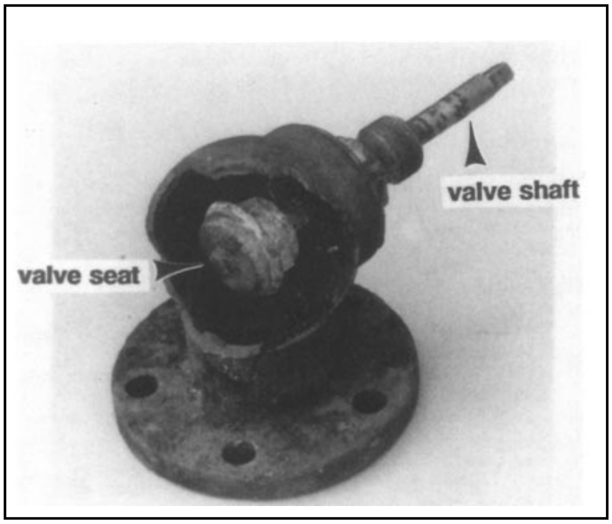

Fig. 1 *The broken tug boat valve in the as-received condition*

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examined using optical (OM) and scanning electron microscopy (SEM). Qualitative chemical analyses were obtained with an energy dispersive spectroscopic (EDS) analyzer on the SEM. These results are reported as the ratio of the peak of maximum intensity of a given element to that of the K_α peak of Cu. The measurements were sufficiently sensitive to distinguish the higher Zn content β phase from the lower Zn content α phase. On the micrographs, OM denotes an optical micrograph and SEM a scanning electron micrograph. Microhardness measurements were made on the as-polished specimen with a load of 2 or 4 kg. The DPH hardness values are accurate to about ±10 DPH.

Results

Microstructural Observations

Figure 3 shows the cross-section of the valve. The columnar grain structure of the seat and shaft show that these were fabricated by casting. They had similar hardnesses. Around the edge of the end of the shaft is a small ring with a different structure and which has a high hardness (294 DPH). This tip was the contact location for the nut. It does not contain columnar grains.

The microstructure of the shaft (Fig. 4) shows the large grains and dendritic structure of a casting. It has interdendritic porosity and is single phase; the valve seat had a similar structure. Optical observations showed that the two parts had a slightly different color, indicating a slightly different Zn content. The microstructure of the nut in Fig. 5 shows that it is in the wrought condition. It contains α and β, and lead particles are also present. These phases are discriminated by the EDS analysis (Fig. 5).

Figure 3 shows that the shaft is held onto the valve seat by the nut by contact with a tip having a

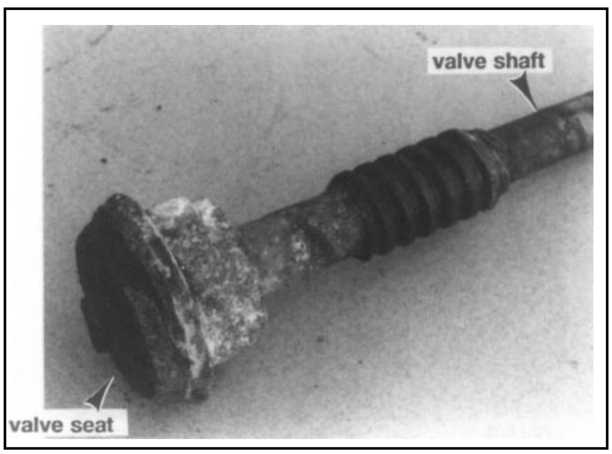

Fig. 2 *The valve seat and shaft assembly in the as-received condition*

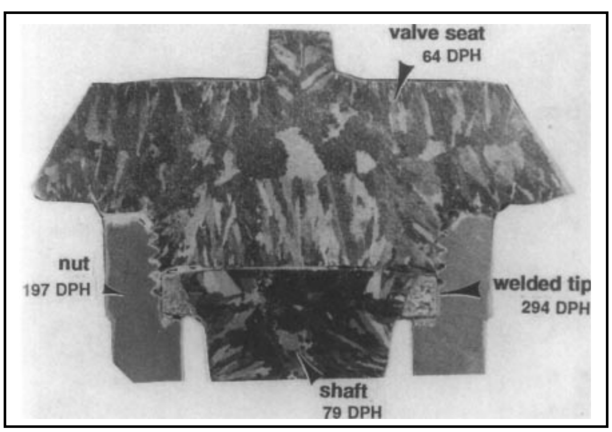

Fig. 3 *Macrograph of the cross section through the assembly*

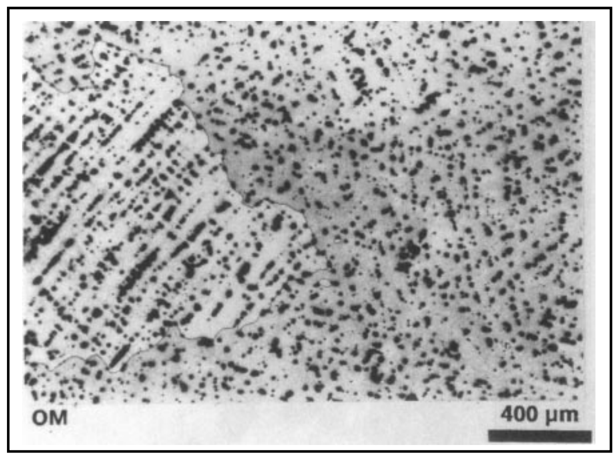

Fig. 4 *Microstructure of the shaft*

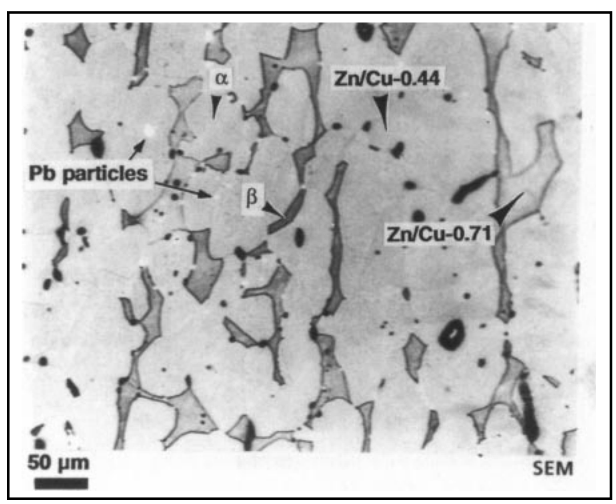

Fig. 5 *Microstructure of the brass nut*

different macrostructure. The interface between these two regions is shown in Fig. 6. It appears that the tip (ring) was welded onto the end of the shaft. The microstructure of this welded tip is shown in Fig. 7. It also consists of α and β phases, with a small amount of Pb particles present.

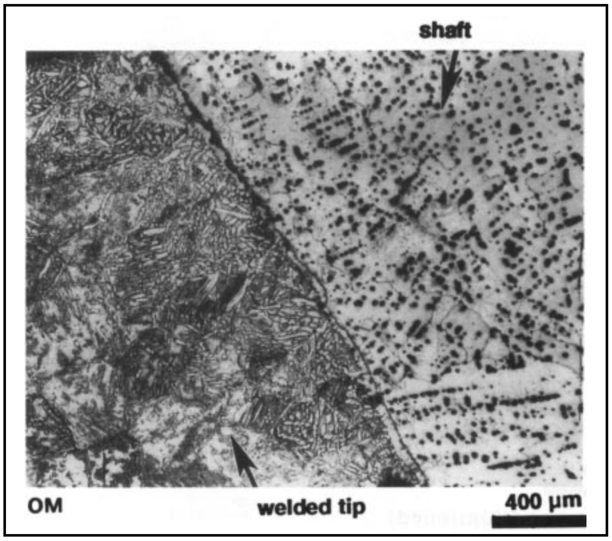

Fig. 6 *Microstructure of the interface between the valve seat and the welded tip*

Zn-Depleted Regions

The cross-section optical microscopy clearly revealed regions along the surfaces that are Cu-colored. These are along both the external and internal surfaces of the nut and the welded tip. The microstructures of some of these regions are shown in Fig. 8. In these regions there is considerable porosity. Figure 9 shows a region of the nut at the surface in which Zn was almost nondetectable. Figure 10 shows a similar region of very high Cu content. Also note that there is a relatively large globular region of Pb. These Pb-rich regions are larger than the Pb particles in the nut at locations remote from the surface (Fig. 7). Figure 10 shows that these Pb regions are made up of what appear to be small Pb particles intertwined with porosity. A strong Cr peak was also obtained from this region.

Figure 11 shows a Zn-depleted region of the welded tip. There is extensive porosity in this region. At the interface separating the unattacked region it is seen that both the α and the β phases are attacked. Figure 12 shows a region of the nut in which the higher copper content β phase is being selectively attacked.

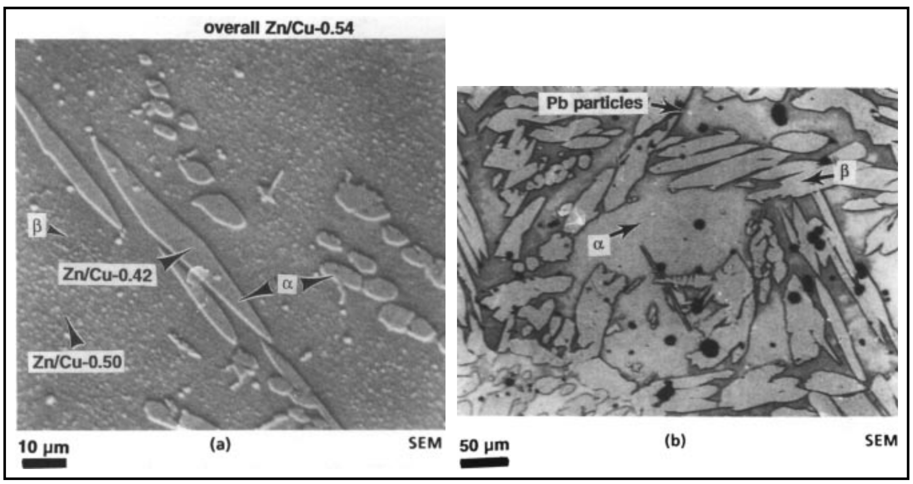

Fig. 7 *Microstructure of the tip welded on the valve seat*

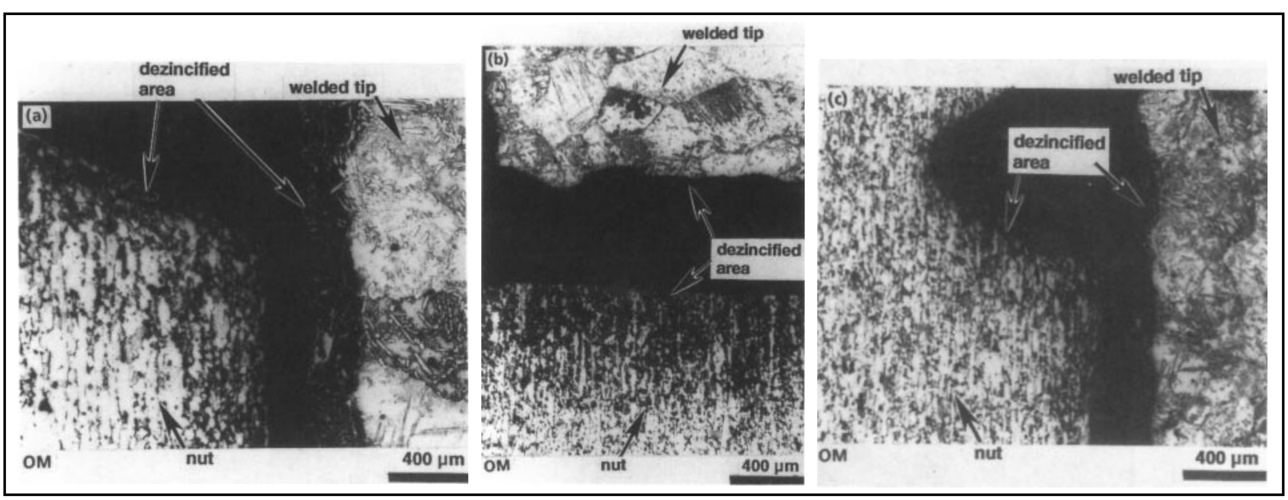

Fig. 8 *Micrographs showing zinc-depleted corrosion regions*

Discussion

General Observations

Brass alloys are commonly used in marine environments for their corrosion resistance (Ref 3). Two types of the two-phase α-β brasses are commonly used: Naval brass and Muntz metal (Ref 4, 5). These both contain about 40% Zn and have similar properties (Ref 5). The Sn bronzes have small (~1%) additions of Sn to improve the corrosion resistance in general (Ref 6) and in salt water (Ref 3). In the EDS analysis, Sn was only rarely detected, but the insensitivity of the technique cannot preclude the possibility that some of the components are made of a Sn-containing brass. It is interesting to note that visual examination of the metallographic sample in Fig. 3 showed that the different regions have slightly different colors, indicating that they are of different compositions.

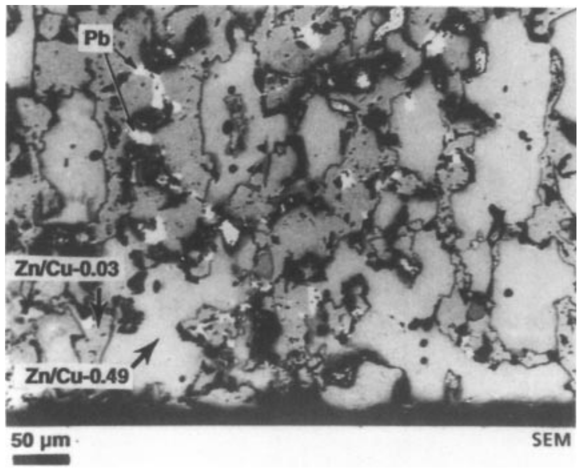

Fig. 9 *Zinc-depleted region in the nut*

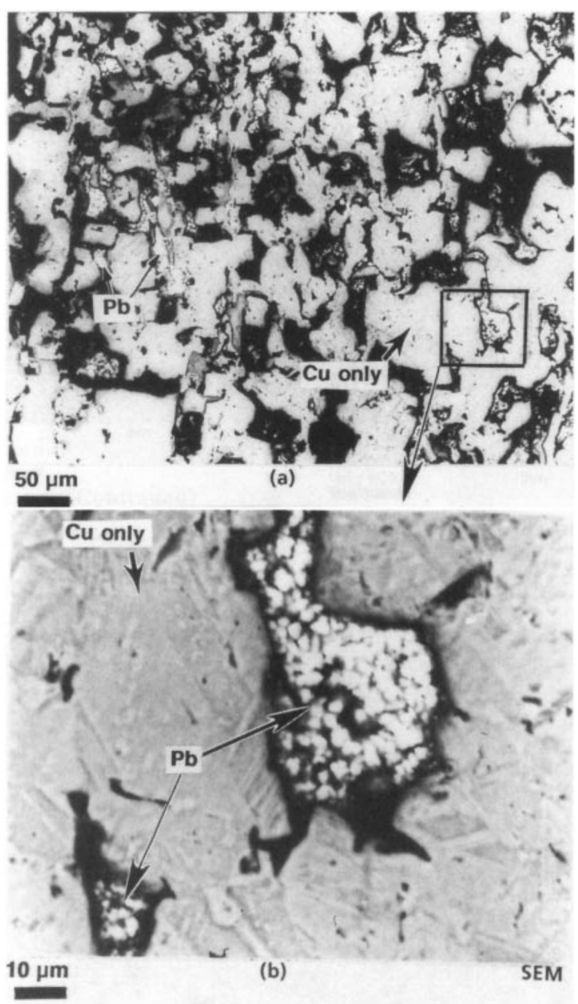

Fig. 10 *Zinc-depleted region in the nut*

The macro- and microstructures show that the valve seat and shaft were cast and both are α brass. The microstructure of the nut shows that it is made from a wrought α-β brass. The ring around the edge of the shaft is of α-β brass, but with a relatively fine structure which has a morphology associated with

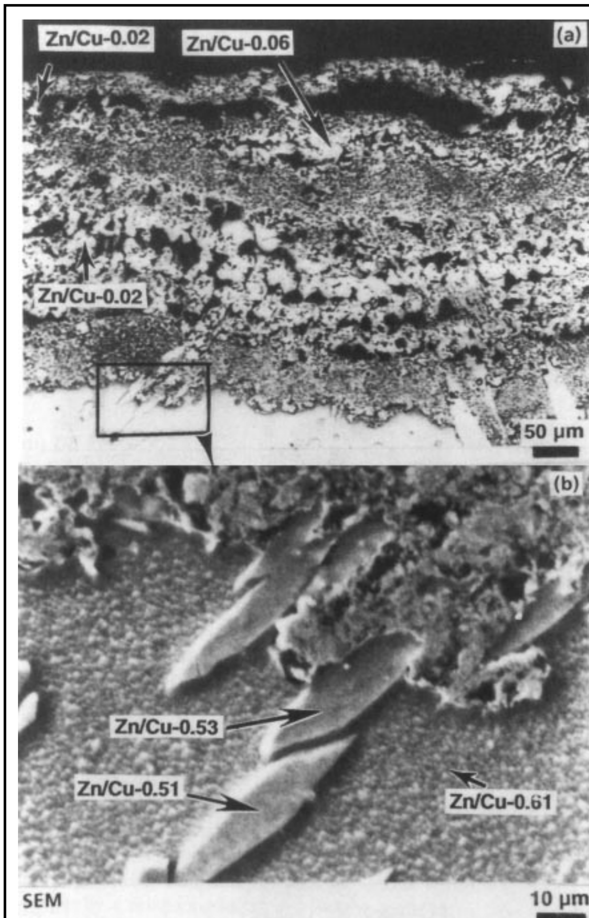

Fig. 11 *Zinc-depleted region in the welded tip of the valve seat*

rapid cooling from high temperature (Ref 7). It appears to be joined by welding. The higher hardness of this ring is associated with its finer structure (Ref 7). It may have been designed originally to serve as a hard region for contact with the nut, or it may have been added to repair a damaged region.

Dezincification

The selective removal of one metallic component in a corrosion process is referred to as dealloying (Ref 8, 9). The process in brass is called dezincification (Ref 8-12), as it is this element which is depleted. Two types of dezincification have been identified in brasses. One is called plug-type, where the process is restricted to a local region. The other is called layer-type, where the surface is attacked more uniformly (Ref 11, 12). It is this latter type that occurred in the brass valve.

It is well known (Ref 6) that the higher Cu content brasses are less susceptible to dezincification.

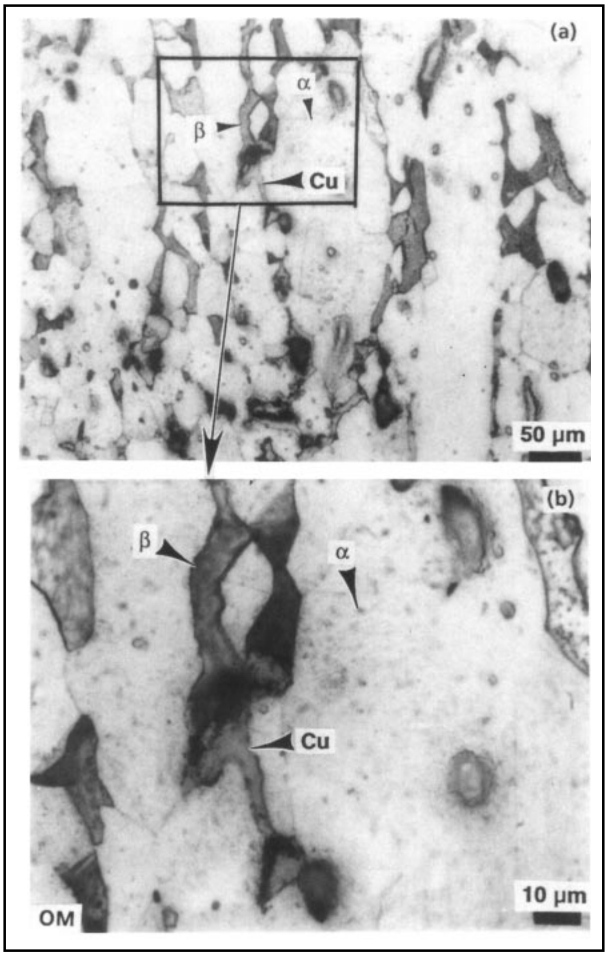

Fig. 12 Zinc-depleted region in the nut showing selective dezincification of the β phase

Consistent with this, no evidence of this type of corrosion was detected in the α brass valve seat and the shaft, but was limited to the higher Zn content, α-β components. The dezincification occurred not only on the external surface of the valve but also on the internal surface, because the construction of the valve assembly allowed the water to contact these surfaces.

In the Cu regions which remained, none or very little Zn was detected (Fig. 10-13). Also, these regions appeared Cu-colored when viewed with an optical microscope. The area in Fig. 12 noted "Cu" is an example of this. In many areas the β phase was clearly being attacked and replaced by Cu, as shown in Fig. 13. In others (Fig. 12) both phases were attacked. Associated with the Cu deposits was porosity, which is commonly found with dezincification (Ref 11, 12).

The nut contained small (e.g., 1 μm) Pb particles (Fig. 5), but in the corroded regions these were much larger (Fig. 9 and 10). It appears that during the solution of the β phase, the small Pb particles dissolved, then redeposited as larger particles. The Cr detected in the lead region of Fig. 10 could be from the etchant used. However, it may be that traces of the more noble Cr in brass were redeposited with the Pb.

In dezincification, it is clear that the Zn goes into solution in the corroding medium, and that Cu remains. However, the mechanism whereby this occurs is not clear (Ref 8, 10). One proposed mechanism is that the Zn dissolves and leaves behind a porous Cu structure (Ref 8). However, since the Zn is in solid solution (in both α and β), its dissolution requires the diffusion of Cu as the remaining Cu densifies in local regions. The other mechanism is that both Zn and Cu dissolve, but that the more noble Cu redeposits (Ref 8) as dense crystals separated by porous regions.

Hummer (Ref 13) has reported the penetration rate of uniform dezincification of Naval brass when immersed in sea water to be about 20 μm per year. Taking the life of the tug, 55 years, as the operating life of the valve, this predicts a corrosion depth of about 1000 μm. Considering the lack of knowledge of the operating life and the corrosion environment of the valve, this value is in reasonable agreement with the typically observed penetration of about 200

μm (see Fig. 9). It appears that the valve had been in service many years.

Conclusions

Dezincification was found on the surfaces of the components of the valve which were made of α-β brass, leaving behind localized regions of essentially pure Cu. No evidence of dezincification was found on the parts made of lower Zn-content α brass, which is consistent with the behavior of brasses in salt water environments. In the α-β brass components, the α brass was usually selectively attacked and replaced with Cu, but at some locations both phases were attacked. Concomitantly with the dezincification, Pb particles which were present in some of the components were apparently dissolved and redeposited as larger particles. The general depth of dezincification is consistent with values predicted from rates reported in the literature for high Zn brasses exposed to salt-containing environments for 55 years, which was the service life of the tug.

Acknowledgments

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